



Occurrence, distribution and risk of organophosphate esters in urban road dust in Beijing, China[☆]



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ARTICLE INFO

Article history:

Received 3 January 2018

Received in revised form

28 April 2018

Accepted 28 May 2018

Keywords:

Organophosphate esters (OPEs)

Road dust

Spatial distribution

Risk assessment

ABSTRACT

As a major group of plasticizers and flame-retardants, organophosphate esters (OPEs) have attracted particular attention due to their wide occurrence and potential impacts on human health and ecosystems. In the present study, the occurrence and distribution of 14 OPEs, including seven Alkyl-OPEs, three Cl-OPEs, and four Aryl-OPEs, were investigated in 65 road dust samples collected from November to December 2014 in Beijing, China. Cl-OPEs were the predominant compounds in the road dust samples, with the median concentration of 646 µg/kg, followed by the Alkyl-OPEs (median 135 µg/kg) and Aryl-OPEs (median 129 µg/kg). Tris(2-chloro-1-methylethyl) phosphate (TCPP) was the most abundant OPE with the median concentration of 384 µg/kg. In addition, OPEs levels showed significant difference ($p < 0.05$) in the spatial distribution. Markedly higher levels of OPEs were observed in 2nd and 3rd ring road with heavy traffic and high population density, indicating that the traffic and population were important factors for this distribution pattern. It was further supported by the analysis of OPEs in roadside soil and indoor dust in the vicinity of road dust sample sites. Finally, the average daily dose (ADD) for OPEs via inhalation, dermal absorption, and ingestion was calculated to evaluate the carcinogenic and non-carcinogenic risks to residents exposed to OPEs in the road dust. Risk assessment revealed that the risk originating from exposure to OPEs of road dust is currently low in Beijing, China.

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1. Introduction

As a major group of plasticizers and flame-retardants, organophosphate esters (OPEs) are widely used in a large variety of consumers' products, including plastics, electronic equipment, textiles, industrial materials and furniture (Hoffman et al., 2017; Reemtsma et al., 2008; Yang et al., 2014). Generally, OPEs are frequently physically mixed with materials as additives rather than chemically bonded to them, and easily released into the surrounding environment (Wei et al., 2015). In addition, they are relatively stable, especially for the chlorinated OPEs which were resistant to be degraded in the environment (Bester, 2005; Meyer and Bester, 2004). So far, OPEs are ubiquitous in the environment and have been frequently detected in various environmental matrices,

including indoor and outdoor air (Möller et al., 2011; Salamova et al., 2014b), surface water (Cristale et al., 2013; Wang et al., 2015), wastewater (Bester, 2005; Marklund et al., 2005a; Martinez-Carballo et al., 2007), drinking water (Andresen and Bester, 2006; Stackelberg et al., 2004), sediment (Cao et al., 2012; Stachel et al., 2005), soil (Fries and Mihajlovic, 2011) and indoor dust samples (Abdallah and Covaci, 2014; Brandsma et al., 2013; Brommer et al., 2012; Kim et al., 2013). However, limited data were available on their occurrence in outdoor dust, especially for the road dust, which is an important source of OPEs in the environment. To our best knowledge, there is only one study focused on the occurrence and distribution of OPEs in urban road dust, in which a single composite road dust sample was collected from main roads of Beijing (Cao et al., 2014).

In general, road dust plays significant roles in the transportation of pollutants from air to other environmental matrices (Brommer et al., 2012). For instance, OPEs in road dust not only can enter groundwater and surface water through rain and surface runoff, but also reenter the atmosphere by wind or volatilization, leading to

[☆] This paper has been recommended for acceptance by B. Nowack.

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water and air pollution (Shi et al., 2013). In addition, OPEs in the dust can also enter the human body by inhalation, ingestion and skin contact, and may pose serious risks to human health (Abdallah and Covaci, 2014; Brommer et al., 2012; Kim et al., 2013). Considering the extensive application of OPEs in vehicles, plastics, hydraulic oils and lubricants, high consumption of these compounds is expected in large urban cities with dense populations and heavy traffic.

It is reported that China is one of the most flame retardants-consuming countries, accounting for approximately 20% of global consumption (EFRA, 2012). Beijing is one of the most developed and populated cities in China, with a huge population of 21.52 million. Besides, now the number of cars in Beijing has dramatically increased to more than 5 million, and huge traffic flow has been observed in this large city. Additionally, many residential areas and commercial buildings are located in the close vicinity of well-established ring road networks, which are characterized with heavy traffic and high population density (Li et al., 2014b). What's more, our previous study has reported that relatively high level of OPEs was observed in road runoff samples collected from the 2nd, 3rd and 4th ring road in the urban of Beijing (Shi et al., 2016). The information of OPEs' occurrence in the dust near ring roads and their health risk is critical.

The aim of this study was to investigate the occurrence, distribution and risk of OPEs in urban road from the densely populated city. Through the observation of 14 OPEs in road dust covering almost the whole urban of Beijing, China, the spatial distribution of the target compounds in road dust was investigated. In addition, roadside soil and house dust samples were collected and analyzed to obtain information on the potential sources of OPEs in road dust. Finally, environmental risk of OPEs in road dust was evaluated to explore the impact of these chemicals on human health.

2. Materials and methods

2.1. Materials and reagents

All solvents (acetonitrile and dichloromethane) were HPLC-grade and purchased from Fisher Scientific (Pittsburgh, PA, USA); Ammonium acetate (99%) was purchased from Alfa Aesar (Miami, OH, USA). Purity water ($>18.2 \text{ M}\Omega \text{ cm}^{-1}$) was prepared with Milli-Q Advantage A10 system (Millipore, Bedford, USA).

Chemical standards of Trimethyl phosphate (TMP, 98.0%), Triethyl phosphate (TEP, 98.0%), Tripropyl phosphate (TPPr, 98.0%), Tri-*n*-butyl phosphate (TnBP, 98.0%), Tri-*iso*-butyl phosphate (TiBP, 98.0%), Tributyoxyethyl phosphate (TBEP, 98.0%), Tri(2-ethylhexyl) phosphate (TEHP, 98.0%), Tri(2-chloroethyl) phosphate (TCEP, 98.0%), Tri(2-chloroisopropyl) phosphate (TCPP, 98.0%), Tris(1,3-dichloro-2-propyl) phosphate (TDCP, 98.0%), Triphenyl phosphate (TPhP, 98.0%), Tri-*m*-cresyl phosphate (TCrP, 98.0%), Cresyldiphenylphosphate (CDPP, 98.0%), and 2-Ethylhexyl diphenyl phosphate (EHDPP, 98.0%) were purchased from Dr. Ehrenstorfer GmbH (Germany). TMP-d₉, TEP-d₁₅ and TPPr-d₂₁ obtained from C/D/N Isotopes Inc. (USA), TPhP-d₁₅ and TnBP-d₂₇ purchased from Cambridge Isotope Laboratories (UK), and TCPP-d₁₈ supported by Toronto Research Chemicals Inc. (Canada) were used as surrogate standards. The physicochemical characteristics of target OPEs are listed in Table S1 in the Supplementary materials.

2.2. Sample collection

A total of 65 dust samples were collected from Beijing ring road (2nd, 3rd, 4th, 5th and 6th ring roads) from November to December

2014 (Fig. 1). Road dust sample was collected with a polyethylene brush and tray, and then transferred into a pre-cleaned polyethylene bag (Yu et al., 2014). After collection, each sample was sieved and the fraction below 200 μm was collected and stored at room temperature. All dust samples were pretreated within one week.

As showed in Fig. 1, the sampling sites A1–A12 belong to 2nd Ring Road ($n = 12$), and sampling sites B1–B11 belong to 3rd Ring Road ($n = 11$), while the samples C1–C14 were collected from 4th Ring Road ($n = 14$), and samples D1–D14 were collected from 5th Ring Road ($n = 15$), samples E1–E13 were collected from 6th Ring Road ($n = 13$). In addition, roadside topsoil ($n = 40$) and indoor dust samples ($n = 17$) were also collected to investigate the potential sources of OPEs in road dust. Soil samples were collected within about 500 m away from the road dust sampling sites. Road soil samples were wrapped in methanol pre-cleaned polyethylene bag, and after being transported to the laboratory all samples were kept at -20°C until pretreatment and analysis. Indoor dust samples were collected from offices ($n = 4$), residential houses ($n = 5$) and dormitories ($n = 8$) and obtained from the surface of floors, furniture and windows with methanol pre-cleaned brushes. The pretreatment procedure for road soil and indoor dust was same as that used for road dust samples.

2.3. Sample preparation

Target compounds were extracted from dust and soil samples and treated by SPE with ENVI-18 cartridges (6 mL, 500 mg; Supelco, USA), as described in our previous study with some modifications (Gao et al., 2016). Briefly, 0.1 g of dry dust samples (1.0 g for soil) were weighed, and 10 ng surrogate standards (TMP-d₉, TEP-d₁₅, TPPr-d₂₁, TPhP-d₁₅, TCPP-d₁₈ and TnBP-d₂₇) were added in samples. After mixing and aging for 24 h, the samples were shaken for 12 h with 10 mL of acetonitrile, and then centrifuged at 4000 r/min. The extract was concentrated to 1 mL under a stream of N_2 at 37°C , diluted to approximately 100 mL with ultrapure water, and then purified by solid phase extraction (SPE) with ENVI-18 cartridges. The cartridges were conditioned with 5 mL acetonitrile and 5 mL ultrapure water sequentially. Then, the extracts were loaded onto the cartridges and rinsed with 6 mL of ultrapure water, dried for 30 min, and eluted with 6 mL 25% DCM in acetonitrile. The eluent was finally concentrated to about 0.4 mL with a stream of nitrogen at 37°C , and diluted to a final volume of 1 mL with ultrapure water. Finally, the concentrate was filtered through a 0.45 μm nylon membrane (Whatman, Maidstone, U.K.), and an aliquot (15 μL) of this solution was injected into the high-performance liquid chromatography-electrospray ionization tandem mass spectrometry (HPLC-ESI MS/MS) system for analysis.

OPEs analysis was performed with an Ultimate 3000 HPLC system (ThermoFisher, USA) coupled to an API 3200 triple-quadrupole mass spectrometer equipped with an electrospray ion source (ESI) (Applied Biosystems/MDS SCIEX, USA). An Acclaim Mixed-Mode HILIC-1 column (2.1 mm \times 150 mm i.d., 5.0 μm , ThermoFisher, USA) was used as the analytical column at a flow rate of 0.25 mL/min. Acetonitrile (A) and pure water (B) were applied as mobile phase, and the gradient program was as follows: the mobile phase starting conditions were 40% of A for 1.0 min, and A was increased to 60% in 4.0 min before being increased to 100% in 3.0 min; 100% of A for 7.0 min, followed by returning to the initial conditions of 40% A in 0.2 min, which was maintained for 6.8 min to allow for equilibration. The total run time was 22.0 min.

The MS system was operated in the positive electrospray ionization and multiple reactions monitoring (MRM) mode. The MS/MS

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